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Abstract. To improve Proton Exchange Membrane Fuel Cells (PEMFC) performances, phenomena occurring in operating conditions must be understood. This work investigates the influence of PTFE (PolyTetraFluoroEthylene) loading in cathodic active layers on the global PEMFC performance and more precisely on diffusive limitations. As they display a controllable pore texture, carbon aerogels may replace advantageously the usual carbon blacks as catalyst support in cathodes. Resulting Membrane Electrode Assemblies (MEA) are evaluated on a monocell test bench. This study shows that PTFE influences greatly PEMFC performances and diffusive limitations as it evacuates the water produced at the cathode. These results highlight that diffusive limitations must be controlled and that PTFE loading must be optimized.

1. Introduction

Due to the rarefaction of fossil fuels and the problem of climate change, researchers are seeking new energy converters that would be suitable. Among the various possibilities are the Proton Exchange Membrane Fuel Cells (PEMFC). They are good candidates for electronic devices or automotive applications thanks to their numerous qualities: low working temperature, quick start-up, etc. However, PEMFC production at a large scale can only be fulfilled provided costs are reduced while power density and durability are increased.

PEMFC electrocatalysts are generally made using carbon blacks as a support. One drawback of these materials is that they do not enable to control the active layer architecture. Consequently, mass-transport hindrances are much often favored. Besides, they do not present an appropriate purity for such electrochemical applications: for example, many carbon blacks contain sulphur, which is a strong poison of Pt catalysts. On the contrary, electrocatalysts based on carbon aerogels and xerogels have a controllable texture (through the synthesis variables of the pristine gel) and are pure materials. They are thus suitable for use in PEMFC electrodes and present good performances [1, 2] depending on the catalytic layer architecture. Moreover, carbon aerogels and xerogels enable a good platinum dispersion thanks to their high specific surface area.

In this study, we analyze diffusive limitations at the cathode active layer using carbon aerogels with a reproducible texture. More precisely, we evaluate the influence of PTFE (PolyTetraFluoroEthylene) loading in the active layer on the performance. The addition of PTFE aims at exhausting water produced at the cathode and reducing electrode flooding. The objectives are (i) to show the impact of PTFE on diffusive limitations and (ii) to improve the PEMFC performance.

2. Experimental Methods

2.1 Carbon aerogels synthesis

Carbon aerogels were prepared following Pekala's method [3]. Gels were obtained by polycondensation of resorcinol (R) with formaldehyde (F) (with a molar ratio F/R=2) and water in the presence of Na_2CO_3 (C). In this study we chose a reagents molar ratio (R/C) equal to 200 and a mass fraction of reagents in the sol of 5 %. After gelation, the gels were placed in successive acetone baths during one week for exchanging water filling the pores of the gels. The gels were then dried under CO_2 supercritical conditions [4, 5]. Afterwards, the dry organic aerogels were pyrolyzed at 1050°C during 30 minutes under a nitrogen flow (5 L/min), thus yielding carbon aerogels.

2.2 Catalyst preparation

Catalysts were prepared using carbon aerogels as catalyst supports. Carbon aerogels were first ground to obtain fine powder (particles *ca*. a few micrometers). Powder samples were then suspended in a H_2PtCl_6 water solution with a platinum concentration of 0.6 g/L and a mass ratio Pt/(Pt+C) equal to 35 wt.%. After 24 h of magnetic stirring, the reducing agent, $NaBH_4$, was added to the suspension as an aqueous solution (0.6 M). $NaBH_4$ was added in large excess and the mixture was mixed during 24 h thus ensuring complete platinum salt reduction. Pt-doped carbon aerogel powder was then washed several times with boiling water, filtered and dried at 100°C for one night. The dry powder obtained was placed in a tubular quartz furnace to undergo thermal treatment. Should platinum salt remain on the carbon surface upon this treatment, we first decomposed it at 350°C under nitrogen flow for 30 minutes and then achieved its reduction by changing nitrogen to hydrogen for 30 minutes. The system cooling was performed under nitrogen flow.

2.3 MEA elaboration

Membrane-Electrode Assemblies (MEA) were realized using the decal method [6]. The cathode catalyst ink was prepared by magnetically stirring Pt-doped carbon aerogel powder, 0.3 wt%-Nafion® solution (dilution with deionized water of DE 1020, Ion Power Inc), PTFE and deionized water. MEAs were prepared with a constant (Nafion®+PTFE)/carbon mass ratio equal to 1 and the amount of PTFE was varied to evaluate its impact on the MEA performance. Catalyst ink was then sprayed on a Kapton® sheet in order to obtain a cathodic Pt loading in the MEA of 0.5 mg/cm² (each cathode had a 50 cm² active geometric surface area). The Kapton® sheet was then hot pressed on a Nafion® N112 membrane with a commercial anode bought from PAXITECH. MEAs were finally obtained by hot-pressing a commercial gas diffusion layer (GDL, carbon felt) and cell gaskets, in a second step. To compare our materials with commercial ones, an MEA was made with a commercial electrocatalyst TKK following the same procedure.

2.4 Fuel cells tests

Experiments were conducted on a homemade air/H_2 monocell test bench [6]. For each MEA, the global performance was evaluated at operating cell temperature of 73°C and pressure of 1.3 bar. Hydrogen and air were used as reactant gases. The relative humidity was kept at 100 % for both gases. A minimum flow rate was applied for the inlet gases when cell intensity is lower than 12 A: 30 NL/h for air and 10 NL/h for hydrogen. The cell was electrically controlled using a potentiostat (Bio-Logic, HCP-803). Each new MEA was submitted to a standard start-up procedure, improving slowly the performance until stabilization. Experimental polarization curves (i.e. E=f(j) plots) were determined by fixing the voltage at chosen values (for increasing and decreasing voltages) and measuring the intensity. For each fixed voltage, the intensity was determined as the average of the two experimental values obtained while increasing or decreasing the voltage and after 5 min stabilization. Impedance spectroscopy and cyclic voltammetry were used to determine the MEA ohmic resistance and the active surface area of platinum respectively. H_2 crossover current density was measured by applying a voltage of 0.5V at the N_2 fed electrode and measuring the oxidation current, the other electrode still being fed with H_2.

3. Results and Discussion

The characteristics of the carbon aerogel used in this study are reported in Table 1. V_{DUB} refers to the microporous volume (pores with a diameter lower than 2 nm). V_p is the porous volume obtained by nitrogen sorption. As our carbon aerogel is macroporous (it contains pores larger than 50 nm), this value is not very accurate. V_{Hg} is the porous volume obtained by mercury porosimetry. $V_{(2\text{-}7.5\ nm)}$ refers to the volume of pores with a diameter between 2 and 7.5 nm. V_v corresponds to the total void volume obtained by combining the results of nitrogen sorption and mercury porosimetry [2].

The carbon aerogel used as catalyst support present a high specific surface area and an important void volume. It contains large mesopores and macropores thus limiting mass-transport hindrances. Its characteristics are suitable for use in PEMFC electrodes as shown by Marie et al. [1].

Table 1. Carbon aerogel characteristics.

%sol	*R/C*	*Specific surface area (m^2/g)*	*V_{DUB} (cm^3/g)*	*V_p (cm^3/g)*	*V_{Hg} (cm^3/g)*	*$V_{(2\text{-}7,5\ nm)}$ (cm^3/g)*	*Vv (cm^3/g)*	*Mean mesopore diameter (nm)*
5	200	649	0.29	3.46	4.6	0.11	5.0	31

The characteristics of our MEA are reported below (Table 2). Four MEAs were elaborated: "PTFE=0" refers to an MEA made without PTFE, "PTFE=0.2" refers to an MEA made with a mass ratio PTFE/Carbon in the cathodic catalytic layer equal to 0.2, "PTFE=0.5" refers to an MEA made with a mass ratio PTFE/Carbon in the cathodic catalytic layer equal to 0.5. TKK corresponds to the MEA made with a commercial electrocatalyst TKK. S_{Pt} refers to the active platinum surface area at the cathode, determined by cyclic voltammetry, and r is the resistance of the MEA, obtained by impedance spectroscopy, both measured in situ.

Table 2. MEA characteristics.

MEA	*Pt/ (Pt+C)* (%)	*Pt loading* (mg/cm^2)	*Nafion®/ Carbon*	*PTFE/ Carbon*	S_{Pt} (m^2/g_{Pt})	*r* (mΩ)	$I_{crossover}$ (mA)	*Tafel slope* (mV/dec)
PTFE=0	35	0.58	1	0	25.4	4.4	82	-97
PTFE=0.2	35	0.56	0.8	0.2	26.3	4.2	78	-85
PTFE=0.5	35	0.53	0.5	0.5	27.1	3.9	81	-84
TKK	26.5	0.58	1	0	92	4.0	147	-79

The MEAs do not have the expected cathodic platinum loading (0.5 mg/cm^2) because of the decal method used to make the cathodic catalyst layers (the obtained platinum loading is superior to the expected value because the catalytic layers were made with an excess of platinum). The addition of PTFE seems to increase a little the active platinum surface area while decreases the Tafel slope. The former phenomena are difficult to explain as PTFE does not conduct protons. For now we can only make hypotheses. The increase of active platinum surface area could originate from the hydrophobic character of PTFE: PTFE would exhaust water to Nafion® which would swell and consequently would get in contact with a more important number of platinum particles. Measurements could also be affected by an effect of pH [7] or impurities in Nafion® [7, 8]. Investigations are in progress to explain these phenomena.

The polarization curves are presented in Figure 1. The use of PTFE improves the fuel cell performance, especially at high current density, but the performance is still lower than that obtained with a commercial electrocatalyst.

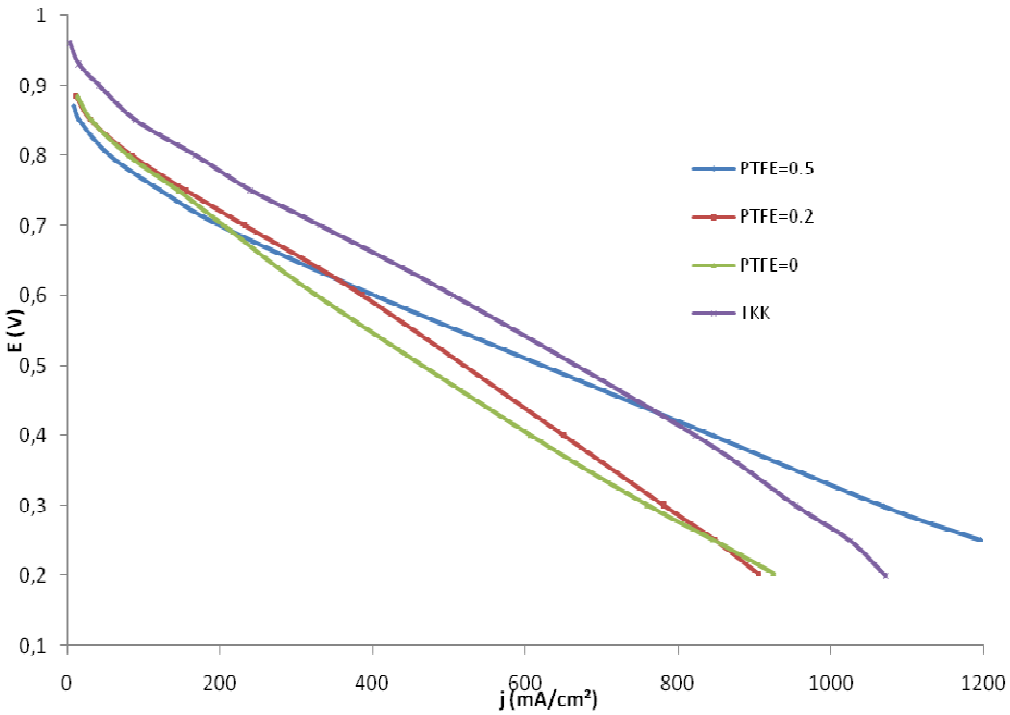

Figure 1: Cell voltage vs. experimental current density for “PTFE=0.5” (blue), “PTFE=0.2” (red), “PTFE=0” (green) and “TKK” (purple).

The cell voltage vs. specific intensity is presented in Figure 2 to determine the impact of platinum loading. In spite of a lower platinum loading in MEA made with PTFE, the performance increases when the PTFE loading increases.

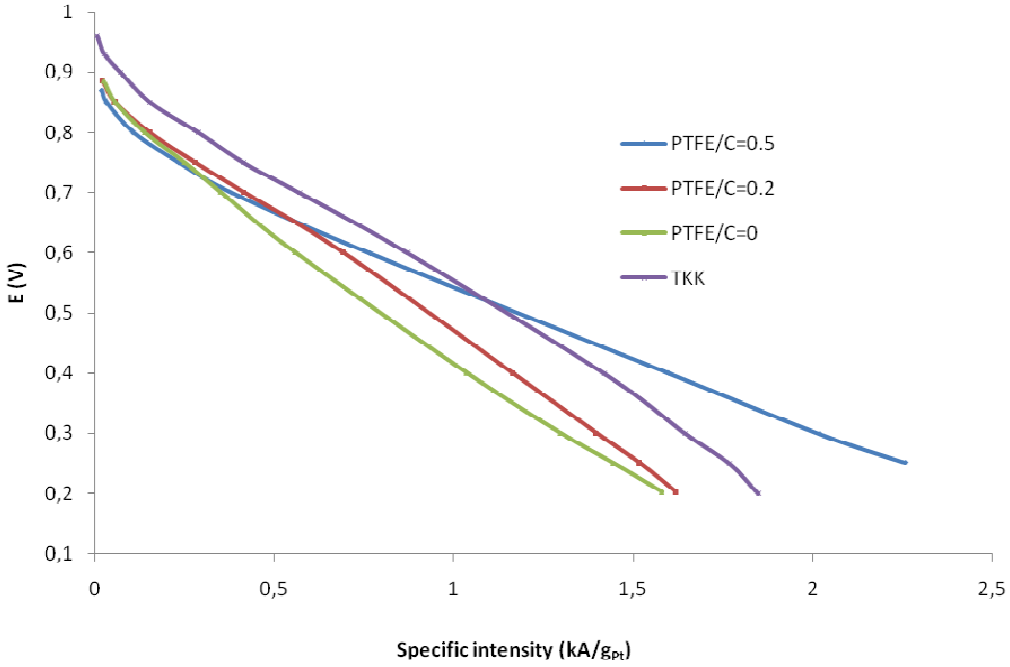

Figure 2: Cell voltage vs. specific intensity for “PTFE=0.5” (blue), “PTFE=0.2” (red), “PTFE=0” (green) and “TKK” (purple).

The MEA performance is analyzed by separating the different contributions to losses. It is well known that the thermodynamic reversible cell potential is diminished by (i) activation losses (η_{ORR}) due to limited O_2 reduction kinetics, (ii) ohmic losses (η_{Ohm}) due to membrane and catalytic layers resistance along with contact quality between the different elements of the cell, (iii) diffusive losses (η_{diff}) due to limited gases and water diffusion in the electrodes. In such systems, activation and diffusion losses in the anode are neglected [1, 9]. Gasteiger et al. [9] have elaborated a methodology to evaluate these different contributions.

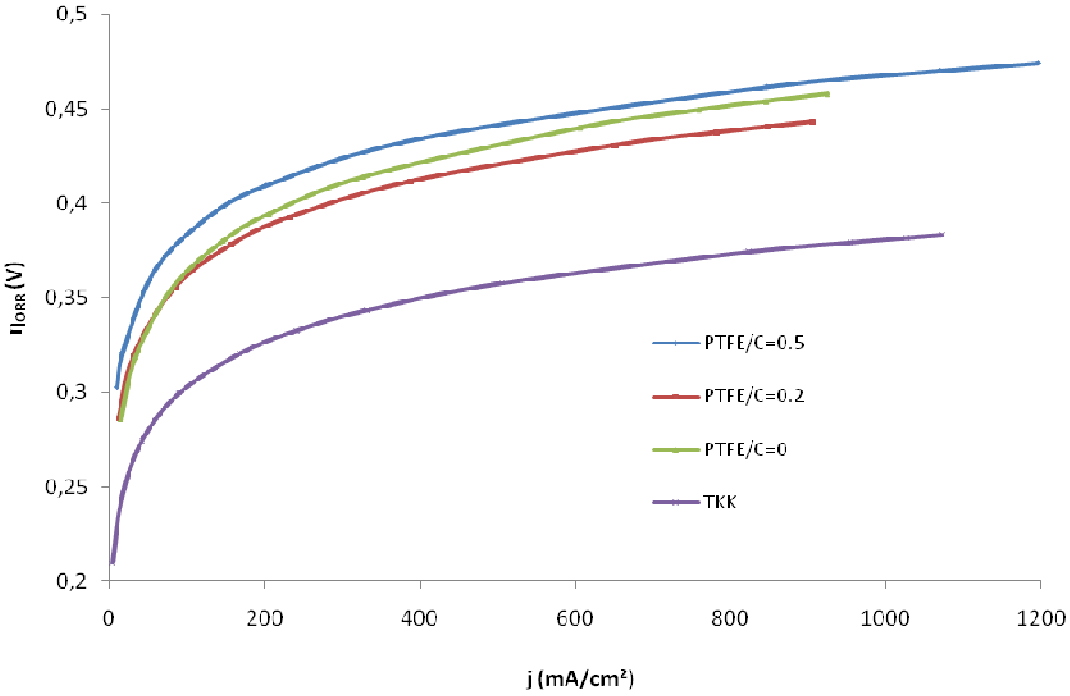

Figure 3: Activation losses vs. experimental current density for "PTFE=0.5" (blue), "PTFE=0.2" (red), "PTFE=0" (green) and "TKK" (purple).

Figure 3 represents the activation losses obtained with the four MEAs. The difference of losses is quite low for MEAs made with the same carbon aerogel. Logically, activation losses are more important when PTFE is included in the catalytic layer since protons cannot circulate in PTFE, but this could also denote for the different mean pH of the active layer with and without PTFE [7] or for different amount of (organic) pollutants brought by these polymers [7, 8]. Besides, activation losses are less important with the commercial electrocatalyst (TKK). Future work will focus on increasing the catalytic activity of our electrocatalysts based on carbon aerogels.

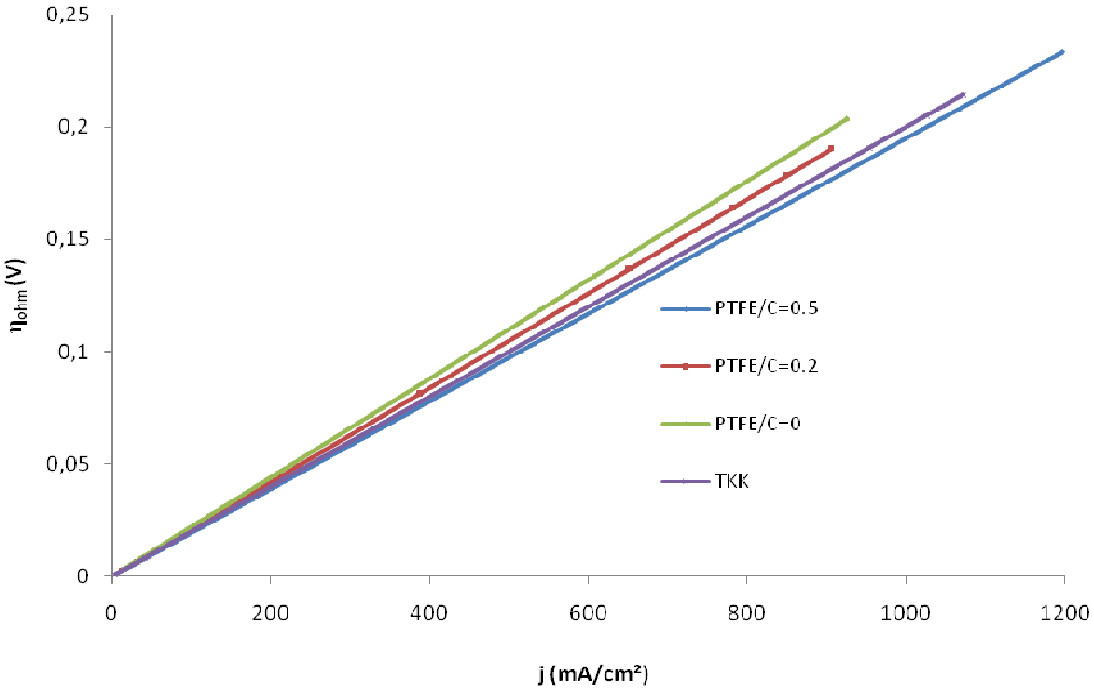

Figure 4: Ohmic losses vs. experimental current density for "PTFE=0.5" (blue), "PTFE=0.2" (red), "PTFE=0" (green) and "TKK" (purple).

As it can be expected from resistance values in Table 2, ohmic losses (Figure 4) are less important in PTFE-loaded catalytic layers. Although this behaviour is expected, because PTFE does not participate in proton conduction, it can also originate the fact that the catalyst loading is not equivalent in the three MEA, thus leading to MEAs with different thicknesses.

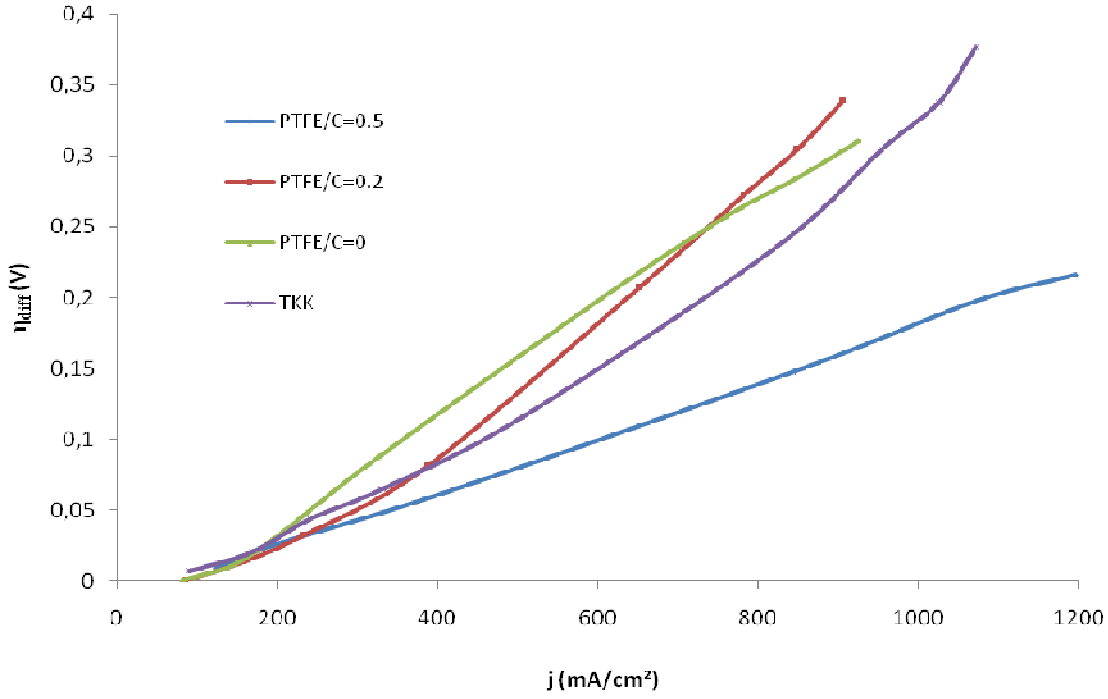

Figure 5: Diffusive losses vs. experimental current density for "PTFE=0.5" (blue), "PTFE=0.2" (red), "PTFE=0" (green) and "TKK" (purple).

Figure 5 represents the diffusive losses obtained with the four MEAs. This graph clearly demonstrates that the beneficial use of PTFE originates from the decrease of diffusive losses. By using PTFE with PTFE/C=0.5, diffusive losses are divided by two with regard to the MEA prepared with the same aerogel as support, without addition of PTFE. This could be explained by the fact that PTFE acts as a drain to exhaust water and as duct to supply gases as noticed by Uchida et al. in a previous work [10]. Besides, in term of diffusive losses, the performance is better than for the commercial electrode.

4. Conclusion

These preliminary results show that PTFE has a big impact on diffusive limitations in PEMFC when using carbon aerogels as catalyst support. By varying the PTFE loading, we demonstrated that PTFE could be beneficial for PEMFC performance. Further investigations are needed to find the optimal amount of PTFE in the catalytic layer. Besides, this study demonstrates how important it is to reduce diffusive limitations as it influences greatly the global performance. In this view, carbon aerogels are very interesting materials: their controllable texture enables to decrease the diffusive limitations. Other parameters can also impact the diffusive limitations like the Nafion® loading or the gas relative humidity. Future work will focus on evaluating the impact of these parameters and on improving the catalytic activity of our electrocatalysts.

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